

APPENDIX B TOXIC SUBSTANCES

B.1 Data for Toxic Substances

The exhibits in this section of Appendix B provide the data needed to carry out the calculations for regulated toxic substances using the methods presented in the text of this guidance. Exhibit B-1 presents data for toxic gases, Exhibit B-2 presents data for toxic liquids, and Exhibit B-3 presents data for several toxic substances commonly found in water solution and for oleum. Exhibit B-4 provides temperature correction factors that can be used to correct the release rates estimated for pool evaporation of toxic liquids that are released at temperatures between 25 °C to 50 °C.

The derivation of the factors presented in Exhibits B-1 - B-4 is discussed in Appendix D. The data used to develop the factors in Exhibits B-1 and B-2 are primarily from Design Institute for Physical Property Data (DIPPR), American Institute of Chemical Engineers, *Physical and Thermodynamic Properties of Pure Chemicals, Data Compilation*. Other sources, including the National Library of Medicine's Hazardous Substances Databank (HSDB) and the *Kirk-Othmer Encyclopedia of Chemical Technology*, were used for Exhibits B-1 and B-2 if data were not available from the DIPPR compilation. The factors in Exhibit B-3 were developed using data primarily from *Perry's Chemical Engineers' Handbook* and the *Kirk-Othmer Encyclopedia of Chemical Technology*. The temperature correction factors in Exhibit B-4 were developed using vapor pressure data derived from the vapor pressure coefficients in the DIPPR compilation.

Exhibit B-1
Data for Toxic Gases

CAS Number	Chemical Name	Molecular Weight	Ratio of Specific Heats	Toxic Endpoint ^a			Liquid Factor Boiling (LFB)	Density Factor (DF) (Boiling)	Gas Factor (GF) ^k	Vapor Pressure @25 °C (psia)	Reference Table ^b
				mg/L	ppm	Basis					
7664-41-7	Ammonia (anhydrous) ^c	17.03	1.31	0.14	200	ERPG-2	0.073	0.71	14	145	Buoyant ^d
7784-42-1	Arsine	77.95	1.28	0.0019	0.6	EHS-LOC (IDLH)	0.23	0.30	30	239	Dense
10294-34-5	Boron trichloride	117.17	1.15	0.010	2	EHS-LOC (Tox ^e)	0.22	0.36	36	22.7	Dense
7637-07-2	Boron trifluoride	67.81	1.20	0.028	10	EHS-LOC (IDLH)	0.25	0.31	28		Dense
7782-50-5	Chlorine	70.91	1.32	0.0087	3	ERPG-2	0.19	0.31	29	113	Dense
10049-04-4	Chlorine dioxide	67.45	1.25	0.0028	1	EHS-LOC equivalent (IDLH) ^g	0.15	0.30	28	24.3	Dense
506-77-4	Cyanogen chloride	61.47	1.22	0.030	12	EHS-LOC equivalent (Tox) ^h	0.14	0.41	26	23.7	Dense
19287-45-7	Diborane	27.67	1.17	0.0011	1	ERPG-2	0.13	1.13	17		Buoyant ^d
75-21-8	Ethylene oxide	44.05	1.21	0.090	50	ERPG-2	0.12	0.55	22	25.4	Dense
7782-41-4	Fluorine	38.00	1.36	0.0039	2.5	EHS-LOC (IDLH)	0.35	0.32	22		Dense
50-00-0	Formaldehyde (anhydrous) ^c	30.03	1.31	0.012	10	ERPG-2	0.10	0.59	19	75.2	Dense
74-90-8	Hydrocyanic acid	27.03	1.30	0.011	10	ERPG-2	0.079	0.72	18	14.8	Buoyant ^d
7647-01-0	Hydrogen chloride (anhydrous) ^c	36.46	1.40	0.030	20	ERPG-2	0.15	0.41	21	684	Dense
7664-39-3	Hydrogen fluoride (anhydrous) ^c	20.01	1.40	0.016	20	ERPG-2	0.066	0.51	16	17.7	Buoyant ⁱ
7783-07-5	Hydrogen selenide	80.98	1.32	0.00066	0.2	EHS-LOC (IDLH)	0.21	0.25	31	151	Dense
7783-06-4	Hydrogen sulfide	34.08	1.32	0.042	30	ERPG-2	0.13	0.51	20	302	Dense
74-87-3	Methyl chloride	50.49	1.26	0.82	400	ERPG-2	0.14	0.48	24	83.2	Dense
74-93-1	Methyl mercaptan	48.11	1.20	0.049	25	ERPG-2	0.12	0.55	23	29.2	Dense
10102-43-9	Nitric oxide	30.01	1.38	0.031	25	EHS-LOC (TLV) ^j	0.21	0.38	19		Dense
75-44-5	Phosgene	98.92	1.17	0.00081	0.2	ERPG-2	0.20	0.35	33	27.4	Dense

Exhibit B-1 (continued)

CAS Number	Chemical Name	Molecular Weight	Ratio of Specific Heats	Toxic Endpoint ^a			Liquid Factor Boiling (LFB)	Density Factor (DF) (Boiling)	Gas Factor (GF) ^k	Vapor Pressure @25 °C (psia)	Reference Table ^b
				mg/L	ppm	Basis					
7803-51-2	Phosphine	34.00	1.29	0.0035	2.5	ERPG-2	0.15	0.66	20	567	Dense
7446-09-5	Sulfur dioxide (anhydrous)	64.07	1.26	0.0078	3	ERPG-2	0.16	0.33	27	58.0	Dense
7783-60-0	Sulfur tetrafluoride	108.06	1.30	0.0092	2	EHS-LOC (Tox ^c)	0.25	0.25 (at -73 °C)	36	293	Dense

Notes:

^a Toxic endpoints are specified in Appendix A to 40 CFR part 68 in units of mg/L. To convert from units of mg/L to mg/m³, multiply by 1,000. To convert mg/L to ppm, use the following equation:

$$Endpoint_{ppm} = \frac{Endpoint_{mg/L} \times 1,000 \times 24.5}{Molecular\ Weight}$$

^b "Buoyant" in the Reference Table column refers to the tables for neutrally buoyant gases and vapors; "Dense" refers to the tables for dense gases and vapors. See Appendix D, Section D.4.4, for more information on the choice of reference tables.

^c See Exhibit B-3 of this appendix for data on water solutions.

^d Gases that are lighter than air may behave as dense gases upon release if liquefied under pressure or cold; consider the conditions of release when choosing the appropriate table.

^e LOC is based on the IDLH-equivalent level estimated from toxicity data.

^f Cannot be liquefied at 25 °C.

^g Not an EHS; LOC-equivalent value was estimated from one-tenth of the IDLH.

^h Not an EHS; LOC-equivalent value was estimated from one-tenth of the IDLH-equivalent level estimated from toxicity data.

ⁱ Hydrogen fluoride is lighter than air, but may behave as a dense gas upon release under some circumstances (e.g., release under pressure, high concentration in the released cloud) because of hydrogen bonding; consider the conditions of release when choosing the appropriate table.

^j LOC based on Threshold Limit Value (TLV) - Time-weighted average (TWA) developed by the American Conference of Governmental Industrial Hygienists (ACGIH).

^k Use GF for gas leaks under choked (maximum) flow conditions.

Issaquah Ammonia Leak Estimate:

The leak was located at a 0.5 inch compression fitting around the outside diameter next to the compression nut. In an attempt to best determine the amount of ammonia released I have converted the annular region around the tubing into an equivalent diameter by estimating the crack around this to be .004 inch around the tube. In doing this, the leak can be modeled by equation below.

Cross sectional area:

$$A_{\text{leak}} = A_{\text{out}} - A_{\text{fitting}}$$

Where

A_{leak} = Area of annular leak space (square inches)

A_{out} = Area of circle whose diameter is .004 inch beyond fitting diameter (square inches)

A_{fitting} = Area of fitting cross section (square inches)

$$A_{\text{out}} = \pi \times d_{\text{out}}^2 / 4 = 3.1416 \times (.5 + .004)^2 / 4 = 0.197136 \text{ sq in}$$

$$A_{\text{fitting}} = \pi \times d_{\text{fitting}}^2 / 4 = 3.1416 \times (.5)^2 / 4 = 0.196350 \text{ sq in}$$

$$A_{\text{leak}} = 0.003154 \text{ sq in}$$

Gaseous Ammonia Release from System:

Source:

Chapter 7.1.1. EPA CEPP Risk Management Program Guidance for Offsite Consequence Analysis
EPA 550-B-99-009, April 1999

$$QR = HA \times P_t \times 1/\sqrt{T_t} \times GF$$

Where

QR = Release rate (pounds per minute)

HA = Hole area (square inches from best estimate) = $A_{\text{leak}} = 0.003154 \text{ sq in}$

P_t = Pressure in system in psia = $135 + 14.7 = 149.7 \text{ psia}$

T_t = Tank temperature (K), where K is absolute temperature in Kelvin = $25 + 273 = 298 \text{ K}$

GF = Gas factor for ammonia (Exhibit B-1 of source document above) = 14

Therefore :

$$QR = 0.003154 \times 149.7 \times 1 / \sqrt{298 \times 14} = 0.212175 \text{ pounds per minute ammonia leak}$$

$$\text{Gas Leak} = 0.38407 \text{ pounds per minute} \times 120 \text{ minutes} = \mathbf{46.1 \text{ pounds}}$$

Observation of liquid loss

Estimated Loss Rate of Ammonia Liquid = 30 Drops / min
at about one ml per drop

Time period of release = 2 hours = 120 minutes

Density of liquid ammonia at boiling point = 682 kg / meter³
and 1 atmosphere

= 0.682 g / ml

One pound = 453 grams

Therefore:

$$\text{Liquid Ammonia release} = (30) \times (0.682) \times (120) / (453) = \mathbf{5.4 \text{ pounds}}$$

Total Release **51.5 pounds**



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7 ESTIMATION OF RELEASE RATES FOR ALTERNATIVE SCENARIOS FOR TOXIC SUBSTANCES

For the alternative scenario analysis, you may use typical meteorological conditions and typical ambient temperature and humidity for your site. This guidance assumes D atmospheric stability and wind speed of 3.0 meters per second (6.7 miles per hour) as conditions likely to be applicable to many sites.

7.1 Release Rates for Toxic Gases

In Section 7.1

- 7.1.1 Methods for unmitigated releases of toxic gases, including:
 - Release of toxic gas from a hole in a tank or pipe (for choked flow conditions, or maximum flow rate),
 - Release of toxic gas from a pipe, based on the flow rate through the pipe, or based on a hole in the pipe (using the same method as for a hole in a tank),
 - Puff releases (no method is provided; users are directed to use other methods),
 - Gases liquefied under pressure, including gaseous releases from holes above the liquid level in the tank and releases from holes in the liquid space, and
 - Consideration of duration of releases of toxic gas.
- 7.1.2 Methods for adjusting the estimated release rate to account for active or passive mitigation, including:
 - Active mitigation to reduce the release duration (e.g., automatic shutoff valves),
 - Active mitigation to reduce the release rate to air, and
 - Passive mitigation (using the same method as for worst-case scenarios).

7.1.1 Unmitigated Releases of Toxic Gases

Gaseous Releases

Gaseous Release from Tank. Instead of assuming release of the entire contents of a vessel containing a toxic gas, you may decide to consider a more likely scenario as developed by the process hazards analysis, such as release from a hole in a vessel or pipe. To estimate a hole size you might assume, for example, the hole size that would result from shearing off a valve or pipe from a vessel containing a regulated substance. If you have a gas leak from a tank, you may use the following simplified equation to estimate a release rate based on hole size, tank pressure, and the properties of the gas. This equation applies to choked flow, or maximum gas flow rate. Choked flow generally would be expected for gases under pressure. (See Appendix D, Section D.6 for the derivation of this equation.)

$$QR = HA \times P_i \times \frac{1}{\sqrt{T_i}} \times GF \quad (7-1)$$

where:	QR	=	Release rate (pounds per minute)
	HA	=	Hole or puncture area (square inches) (from hazard evaluation or best estimate)
	P_i	=	Tank pressure (pounds per square inch absolute (psia)) (from process information; for liquefied gases, equilibrium vapor pressure at 25 °C is included in Exhibit B-1, Appendix B)
	T_i	=	Tank temperature (K), where K is absolute temperature in kelvins; 25 °C (77 °F) is 298 K
	GF	=	Gas Factor, incorporating discharge coefficient, ratio of specific heats, molecular weight, and conversion factors (listed for each regulated toxic gas in Exhibit B-1, Appendix B)

You can estimate the hole area from the size and shape of the hole. For a circular hole, you would use the formula for the area of a circle (area = πr^2 , where π is 3.14 and r is the radius of the circle; the radius is half the diameter).

This equation will give an estimate of the initial release rate. It will overestimate the overall release rate, because it does not take into account the decrease in the release rate as the pressure in the tank decreases. You may use a computer model or another calculation method if you want a more realistic estimate of the release rate. As discussed below, you may use this equation for releases of gases liquefied under pressure if the release would be primarily gas (e.g., if the hole is in the head space of the tank, well above the liquid level).

Example 19. Release of Toxic Gas from Tank (Diborane)

You have a tank that contains diborane gas at a pressure of 30 psia. The temperature of the tank and its contents is 298 K (25 °C). A valve on the side of the tank shears off, leaving a circular hole 2 ½ inches in diameter in the tank wall. You estimate the area from the formula for area of a circle (πr^2 , where r is the radius). The radius of the hole is 1 ¼ inches, so the area is $\pi \times (1 \frac{1}{4})^2$, or 5 square inches. From Exhibit B-1, the Gas Factor for diborane is 17. Therefore, the release rate, from Equation 7-1, is:

$$QR = 5 \times 30 \times 1/(298)^{1/2} \times 17 = 148 \text{ pounds per minute}$$

Gaseous Release from Pipe. If shearing of a pipe may be an alternative scenario for a toxic gas at your site, you could use the usual flow rate through the pipe as the release rate and carry out the estimation of distance as discussed in Chapter 8.

If you want to consider a release of toxic gas through a hole in a pipe as an alternative scenario, you may use the method described above for a gas release from a hole in a tank. This method neglects the effects of friction along the pipe and, therefore, provides a conservative estimate of the release rate.

Puff Releases. If a gaseous release from a hole in a tank or pipe is likely to be stopped very quickly (e.g., by a block valve), resulting in a puff of toxic gas that forms a vapor cloud rather than a plume, you may want to consider other methods for determining a consequence distance. A cloud of toxic gas resulting from a puff release will not exhibit the same behavior as a plume resulting from a longer release (e.g., a release over 10 minutes).

Liquefied Gases

Gases Liquefied Under Pressure. Gases liquefied under pressure may be released as gases, liquids, or a combination (two-phase), depending on a number of factors, including liquid level and the location of the hole relative to the liquid level. The resulting impact distances can vary greatly.

For releases from holes above the liquid level in a tank of gas liquefied under pressure, the release could be primarily gas, or the release may involve rapid vaporization of a fraction of the liquefied gas and possibly aerosolization (two-phase release). It is complex to determine which type of release (i.e., gas, two-phase) will occur and the likely mix of gases and liquids in a two-phase release. The methods presented in this guidance do not definitively address this situation. As a rule of thumb, if the head space is large and the distance between the hole and the liquid level is relatively large given the height of the tank or vessel, you could assume the release is gaseous and, therefore, use Equation 7-1 above. (Exhibit B-1, Appendix B, includes the equilibrium vapor pressure in psia for listed toxic gases liquefied under pressure at 25 °C; this pressure can be used in Equation 7-1.) However, use of this equation will not be conservative if the head space is small and the release from the hole is two-phased. In situations where you are unsure of whether the release would be gaseous or two-phase, you may want to consider other models or methods to carry out a consequence analysis.

For a hole in the liquid space of a tank, you may use Equation 7-2 below to estimate the release rate. Exhibit B-1 in Appendix B gives the equilibrium vapor pressure in psia for listed toxic gases at 25 °C; this is the pressure required to liquefy the gas at this temperature. You can estimate the gauge pressure in the tank from the equilibrium vapor pressure by subtracting the pressure of the ambient atmosphere (14.7 psi). Exhibit B-1 also gives the Density Factor (DF) for each toxic gas at its boiling point. This factor can be used to estimate the density of the liquefied gas (the density at 25 °C would not be significantly different from the density at the boiling point for most of the listed gases). The equation to estimate the release rate is (see Appendix D, Section D.7.1, for more information):

$$QR = HA \times 6.82 \sqrt{\frac{11.7}{DF^2} \times LH + \frac{669}{DF} \times P_g} \quad (7-2)$$

where:	QR	=	Release rate (pounds per minute)
	HA	=	Hole or puncture area (square inches) (from hazard evaluation or best estimate)
	DF	=	Density Factor (listed for each regulated toxic gas in Exhibit B-1, Appendix B; $1/(DF \times 0.033)$ is density in pounds per cubic foot)
	LH	=	Height of liquid column above hole (inches) (from hazard evaluation or best estimate)
	P_g	=	Gauge pressure of the tank pressure (pounds per square inch gauge (psig), from vapor pressure of gas (listed in Exhibit B-1, Appendix B) minus atmospheric pressure (14.7 psi)

This equation gives the rate of release of liquid through the hole. For a gas liquefied under pressure, assume that the released liquid will immediately flash into vapor (or a vapor/aerosol mixture) and the release rate to air is the same as the liquid release rate. This equation gives an estimate of the initial release rate. It will overestimate the overall release rate, because it does not take into account the decrease in the release rate as the pressure in the tank and the height of the liquid in the tank decrease. You may use a computer model or another calculation method if you want a more realistic estimate of the release rate.

For a release from a broken pipe of a gas liquefied under pressure, see equations 7-4 to 7-6 below for liquid releases from pipes. Assume the released liquid flashes into vapor upon release and use the calculated release rate as the release rate to air.

Gases Liquefied by Refrigeration. Gases liquefied by refrigeration alone may be treated as liquids. You may use the methods described in Section 7.2 for estimation of release rates.

Duration of Release

The duration of the release is used in choosing the appropriate generic reference table of distances, as discussed in Chapter 8. (You do not need to consider the duration of the release to use the chemical-specific reference tables.) You may calculate the maximum duration by dividing the quantity in the tank or the quantity that may be released from pipes by your calculated release rate. You may use 60 minutes as a default value for maximum release duration. If you know, and can substantiate, how long it is likely to take to stop the release, you may use that time as the release duration.

7.1.2 Mitigated Releases of Toxic Gases

For gases, passive mitigation may include enclosed spaces, as discussed in Section 3.1.2. Active mitigation for gases, which may be considered in analyzing alternative release scenarios, may include an assortment of techniques including automatic shutoff valves, rapid transfer systems (emergency deinventory), and water/chemical sprays. These mitigation techniques have the effect of reducing either the release rate or the duration of the release, or both.

Active Mitigation

Active Mitigation to Reduce Release Duration. An example of a mitigation technique to reduce the release duration is automatic shutoff valves. If you have an estimate of the rate at which the gas will be released and the time it will take to shut off the release, you may estimate the quantity potentially released (release rate times time). You must be able to substantiate the time it will take to shut off the release. If the release will take place over a period of 10 minutes or more, you may use the release rate to estimate the distance to the toxic endpoint, as discussed in Chapter 8. For releases stopped in less than 10 minutes, multiply the initial release rate by the duration of release to estimate the quantity released, then divide the new quantity by 10 minutes to estimate a mitigated release rate that you may apply to the reference tables described in Chapter 8 to estimate the consequence distance. If the release would be stopped very quickly, you might want to consider other methods that will estimate consequence distances for a puff release.

Active Mitigation to Directly Reduce Release Rate to Air. Examples of mitigation techniques to directly reduce the release rate include scrubbers and flares. Use test data, manufacturer design specifications, or past experience to determine the fractional reduction of the release rate by the mitigation technique. Apply this fraction to the release rate that would have occurred without the mitigation technique. The initial release rate, without mitigation, may be the release rate for the alternative scenario (e.g., a release rate estimated from the equations presented earlier in this section) or the worst-case release rate. The mitigated release rate is:

$$QR_R = (1 - FR) \times QR \quad (7-3)$$

where:

QR_R	=	Reduced release rate (pounds per minute)
FR	=	Fractional reduction resulting from mitigation
QR	=	Release rate without mitigation (pounds per minute)

Example 20. Water Spray Mitigation (Hydrogen Fluoride)

A bleeder valve on a hydrogen fluoride (HF) tank opens, releasing 660 pounds per minute of HF. Water sprays are applied almost immediately. Experimental field and laboratory test data indicate that HF vapors could be reduced by 90 percent. The reduced release rate is:

$$\begin{aligned} QR_R &= (1 - 0.9) \times (660 \text{ pounds per minute}) \\ &= 66 \text{ pounds per minute} \end{aligned}$$

In estimating the consequence distance for this release scenario, you would need to consider the release both before and after application of the water spray and determine which gives the greatest distance to the endpoint. You need to be able to substantiate the time needed to begin the water spray mitigation.